Interfacial Segregation in Oxide Ceramics: Atomic-Scale Experimental and Theoretical Studies (DMR-0196563-Ceramics)

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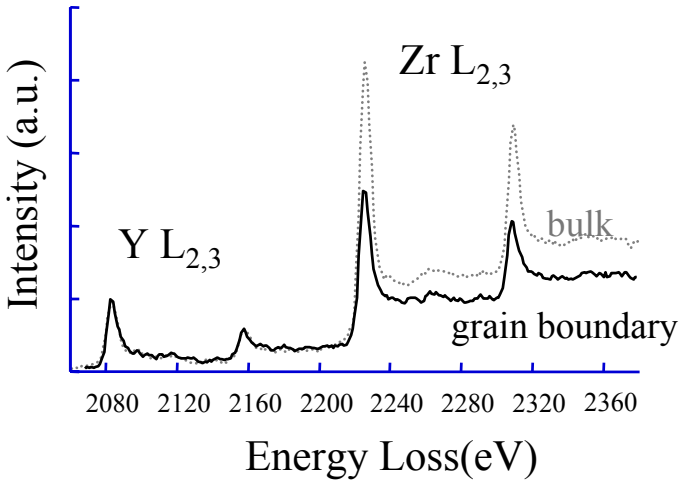
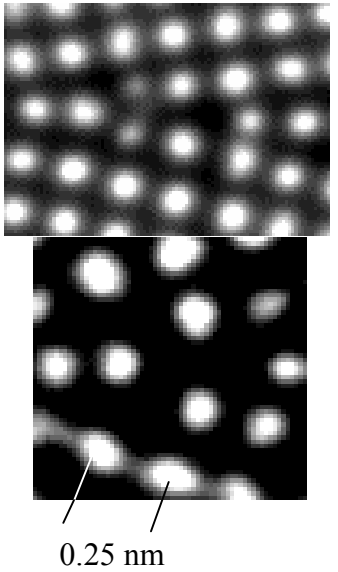


Y^{3+} segregation to grain boundaries quantified by electron energy loss spectroscopy

Core structures of 24˚ and 36˚ (100) grain boundaries in yttria-stabilized cubic zirconia were determined by Z-contrast scanning transmission electron microscopy.



Density functional theory was used to refine atomic coordinates of the 36˚ grain boundary and identify preferred sites for Y^{3+} segregation (identified by white circle)

“"Structure and Chemistry of Yttria-stabilized Cubic Zirconia Symmetrical Tilt Grain Boundaries," *Journal of the American Ceramic Society,* **84** (2001) 1361-1368.
“Ab-initio Calculations of Pristine and Doped Σ5 (310)/[001] ZrO_2 Grain Boundaries”, Z. Mao, S.B. Sinnott, and E.C. Dickey, *Journal of the American Ceramic Society* **85** (2002) 1594-1600.

The goal of this program is to develop an experimentally- and theoretically-based atomic scale understanding of segregation phenomena in oxide ceramics. Zirconia bicrystals were taken as model systems since it is known that transport properties are greatly altered by segregation of defects to the grain boundaries. In fact, it has been shown in previous literature that the grain boundary resistivity is 100 times higher than in the bulk.

The upper right hand figure contains two high-resolution Z-contrast images of the 24˚ (upper) and 36˚ (lower) symmetric tilt (100) grain boundaries in ytrria-stabilized cubic zirconia (YSZ). The bright spots are projected cation columns. From the experimental data atomic models of the grain boundary cores were developed.

The left hand figure shows electron energy loss spectra (EELS) acquired from bulk YSZ and locally at the 36˚ grain boundary core. From the data, an excess of 4.9 atoms/cm^2 of Y^{3+} at the grain boundary was quantified.

The experimentally derived model of the 36˚ boundary was used as the basis for density functional theory calculations which were used to relax the structure and to calculate grain boundary energies and defect segregation energies. Excellent agreement between the relaxed structure and experimental data are observed in the overlaid structures in figure. The pristine (undoped) grain boundary energy was determined to be 0.04 ev/Å^2. Segregation energies of Y^{3+} were calculated for various grain boundary sites, and the lowest was that identified with the white circle at -13.8 eV/atom.